UNIVERSITI SAINS MALAYSIA

Final Examination
2015/2016 Academic Session

May/June 2016

JIK 419 – Advanced Organic Chemistry
[Kimia Organik Lanjutan]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains **ELEVEN** printed pages before you begin the examination.

Answer **FIVE** questions. You may answer **either** in Bahasa Malaysia or in English.

All answers must be written in the answer booklet provided.

Each question is worth 20 marks and the mark for each sub question is given at the end of that question.

In the event of any discrepancies in the exam questions, the English version shall be used.

*Sila pastikan bahawa kertas peperiksaan ini mengandungi **SEBELAS** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA** soalan. Anda dibenarkan menjawab soalan **sama ada** dalam Bahasa Malaysia atau Bahasa Inggeris.*

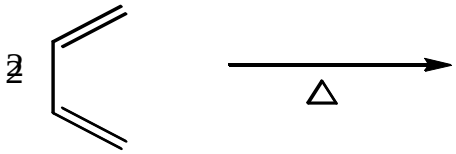
Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

1. (a) Draw the structure of the product(s) for each of the following reaction.
Lukiskan struktur hasil/hasil-hasil untuk setiap tindak balas berikut.

(i)



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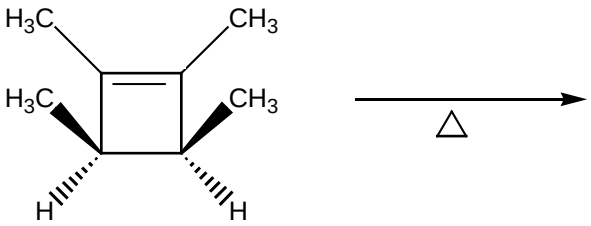

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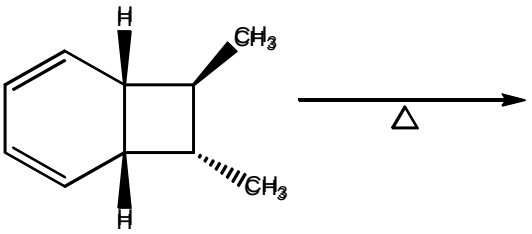

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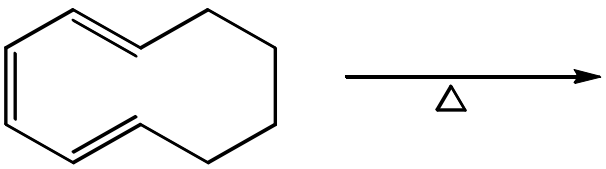
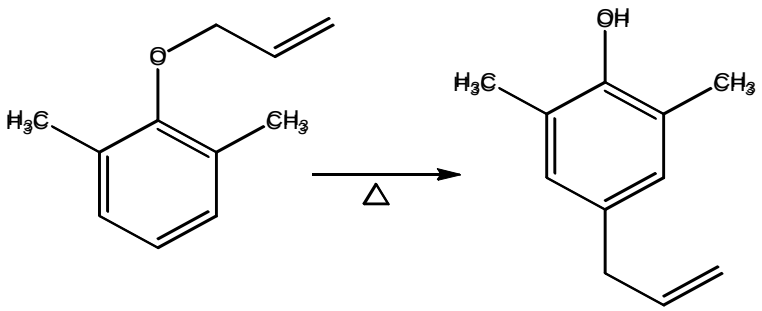


(8 marks/*markah*)

(b) Propose a mechanism for the following reaction:

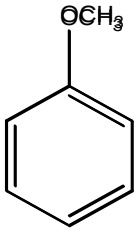
Cadangkan satu mekanisme untuk tindak balas berikut:



(6 marks/*markah*)

(c) Propose product(s) and mechanism for the $AlCl_3$ catalysed reaction of methyl chloride with anisole.

Cadangkan hasil/hasil-hasil dan mekanisme untuk tindak balas pemangkinan $AlCl_3$ metil klorida dengan anisol.



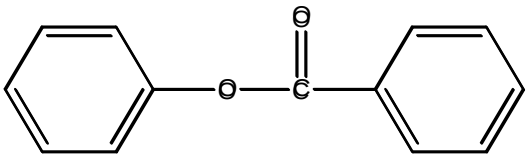
Anisole

(6 marks/*markah*)

2. (a) Draw the structure of the product(s) obtained from the reaction of each of the following compounds with $Br_2/FeBr_3$:

Lukiskan struktur hasil/hasil-hasil yang diperolehi daripada setiap tindak balas sebatian berikut dengan $Br_2/FeBr_3$:

(i)



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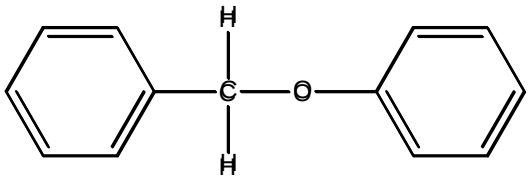

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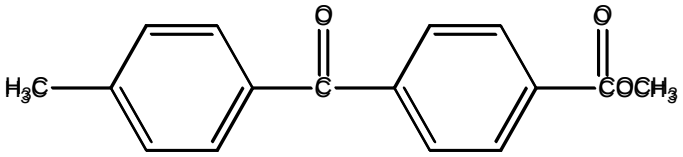

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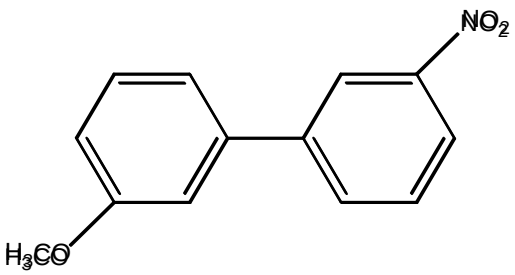
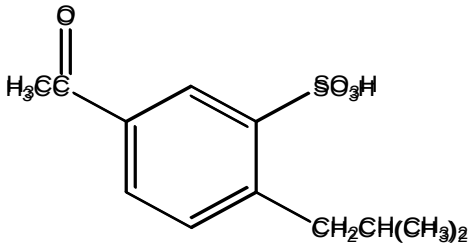


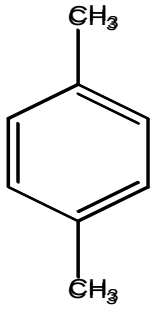
(8 marks/*markah*)

(b) Show how the following compound could be prepared from benzene:
Tunjukkan bagaimana sebatian berikut dapat disediakan daripada benzena:



(8 marks/*markah*)

(c) *p*-Xylene undergoes nitration much faster than benzene. Use resonance forms of the sigma complex to explain this accelerated rate.
p-Xilena mengalami penitratan lebih cepat daripada benzena. Gunakan bentuk resonans sigma kompleks untuk menerangkan kadar kelajuan ini.

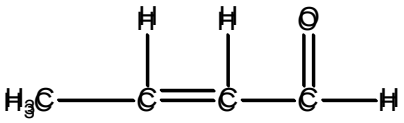


p-Xylene

(4 marks/*markah*)

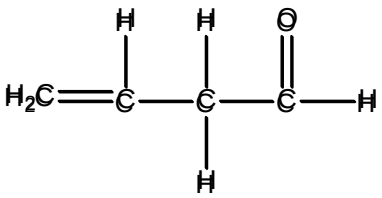
3. (a) In each of the following compounds, indicate the most acidic hydrogen. Draw the important resonance contributors of the anion that results from removal of the most acidic hydrogen.
Dalam setiap sebatian berikut, tunjukkan hidrogen yang paling berasid. Lukiskan penyumbang resonans anion yang penting terhasil daripada penyingkiran hidrogen yang paling berasid.

(i)



(4 marks/*markah*)

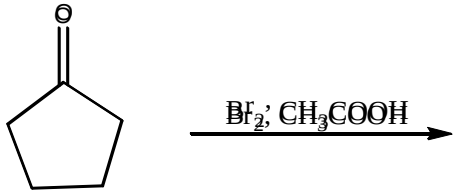
(ii)



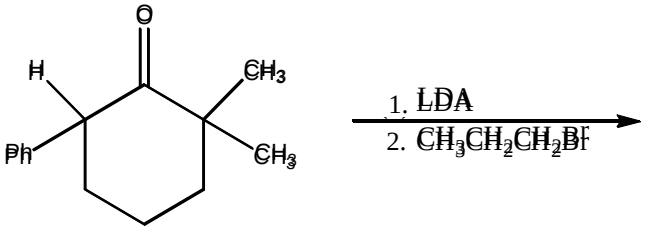
(4 marks/*markah*)

(b) Draw the structure of the product(s) for each of the following reaction.
Lukiskan struktur hasil/hasil-hasil untuk setiap tindak balas berikut.

(i)

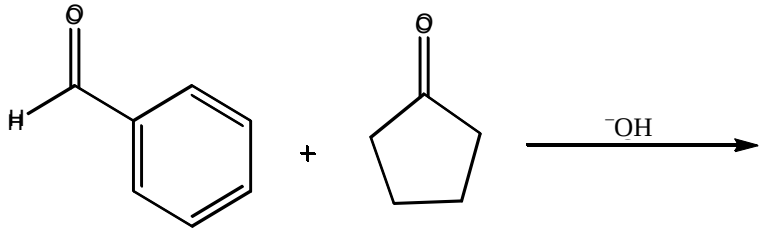


(ii)

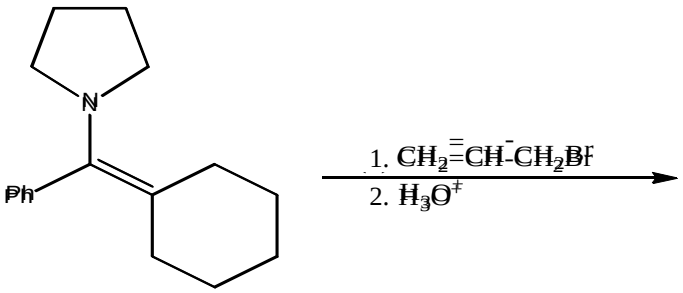


LDA = Lithium Diisopropylamide

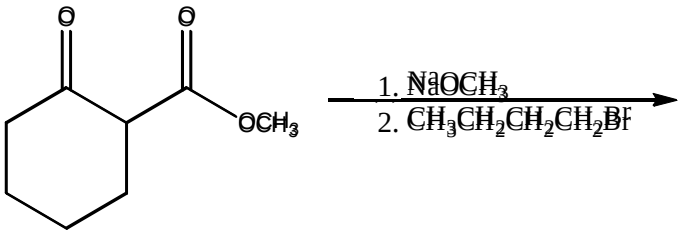
(iii)



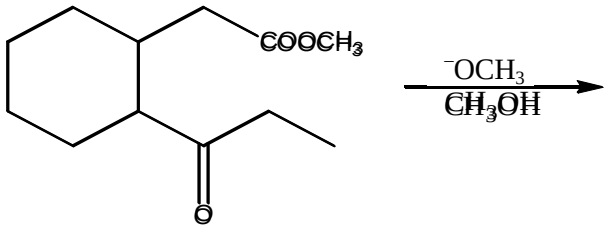
(iv)



(v)



(vi)



(12 marks/*markah*)

4. (a) An unknown reducing disaccharide is found to be unaffected by invertase enzymes. Treatment with an α-galactosidase cleaves the disaccharide to give one molecule of D-fructose and one molecule of D-galactose. When the disaccharide is treated with excess iodomethane and silver oxide and then hydrolyzed in dilute acid, the products are 2,3,4,6-tetra-*O*-methylgalactose and 1,3,4-tri-*O*-methylfructose. Propose a structure for this disaccharide, and give its complete systematic name.

Suatu disakarida penurun didapati tidak terjejas oleh enzim invertas. Olahan dengan α-galaktosidas memutuskan disakarida itu menghasilkan satu molekul D-fruktosa dan satu molekul D-galaktosa. Apabila disakarida itu diolahkan dengan iodometana berlebihan dan argentum oksida dan seterusnya dihidrolisis dalam asid cair menghasilkan 2,3,4,6-tetra-O-metilgalaktosa dan 1,3,4-tri-O-metilfruktosa. Cadangkan satu struktur bagi disakarida ini, dan berikan nama sistematik lengkapnya.

(6 marks/*markah*)

(b) D-Lyxose is formed by Ruff degradation of galactose. Give the structure of D-lyxose. Ruff degradation of D-lyxose gives D-threose. Give the structure of D-threose.

D-Liksosa dibentukkan oleh galaktosa dari degredasi Ruff. Berikan struktur D-liksosa. Degredasi Ruff dari D-liksosa memberikan D-treosa. Berikan struktur D-treosa.

(4 marks/*markah*)

(c) Propose a mechanism for the base catalysed epimerisation of erythrose to a mixture of erythrose and threose.

Cadangkan suatu mekanisme pengepimeran eritrosa bermangkinkan bes untuk menghasilkan campuran eritrosa dan treosa.

(6 marks/*markah*)

(d) What is the main structural difference between:

(i) amylose and cellulose

(ii) amylose and amylopectin

Apakah perbezaan utama antara struktur:

(i) amilosa dan selulosa

(ii) amilosa dan amilopektin

(4 marks/*markah*)

5. (a) Draw the structure of the product(s) that are obtained when D-galactose reacts with the following:

(i) Nitric acid

(ii) Tollens' reagent

(iii) H_2/Ni

(iv) Excess phenylhydrazine

(v) Br_2 in water

Lukiskan struktur hasil/hasil-hasil yang diperolehi apabila D-galaktosa bertindak balas dengan reagen berikut:

(i) *Asid nitrik*

(ii) *Reagen Tollens'*

(iii) *H_2/Ni*

(iv) *Fenilhidrazin berlebihan*

(v) *Br_2 dalam air*

(10 marks/*markah*)

(b) Show how you would use solution phase synthesis to make tripeptide Ile−Gly−Asn.

Tunjukkan bagaimana anda menggunakan sintesis fasa larutan untuk menyediakan tripeptida Ile-Gly-Asn.

(10 marks/*markah*)

6. (a) Calculate the isoelectric point (p*I*) for:

(i) Asparagine $\left(\mathrm{p}K_{a_1} = 2.02, \mathrm{p}K_{a_2} = 8.84\right)$

(ii) Arginine $\left(\mathrm{p}K_{a_1} = 2.17, \mathrm{p}K_{a_2} = 9.04, \mathrm{p}K_{a_3} = 12.48\right)$

$\mathrm{p}K_{a_3}$ belongs to the side chain group

Kira takat isoelektrik (pI) untuk:

(i) *Asparagina* $\left(\mathrm{p}K_{a_1} = 2.02, \mathrm{p}K_{a_2} = 8.84\right)$

(ii) *Arginina* $\left(\mathrm{p}K_{a_1} = 2.17, \mathrm{p}K_{a_2} = 9.04, \mathrm{p}K_{a_3} = 12.48\right)$

$\mathrm{p}K_{a_3}$ *tergolong dalam kumpulan rantai sisi*

(4 marks/*markah*)

(b) Draw the structure of the predominant form of:

(i) Aspartic acid at pH 7

(ii) Glutamine at pH 7

Lukiskan struktur bagi bentuk yang paling predominan:

(i) Asid aspartik pada pH 7

(ii) Glutamina pada pH 7

(4 marks/*markah*)

(c) Show how you would use the Gabriel-Malonic ester synthesis to make histidine.

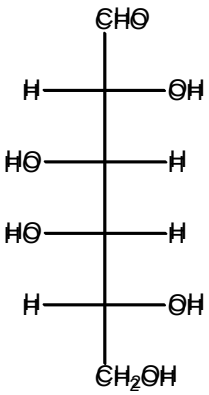
Tunjukkan bagaimana anda menggunakan sintesis ester Gabriel-Malonik untuk menyediakan histidina.

(6 marks/*markah*)

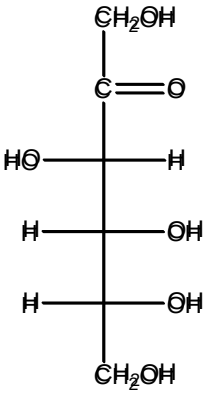
(d) Show how you would use the Strecker synthesis to make valine.

Tunjukkan bagaimana anda menggunakan sintesis Streckar untuk menyediakan valina.

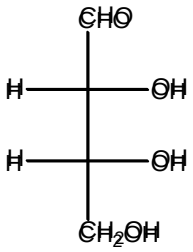
(6 marks/*markah*)



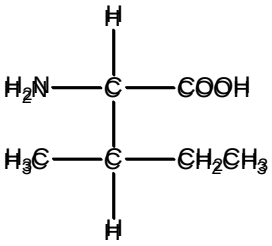
D-Galactose



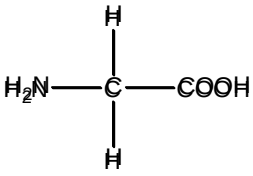
D-Fructose



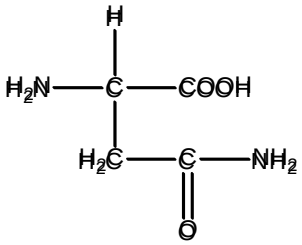
D-Erythrose



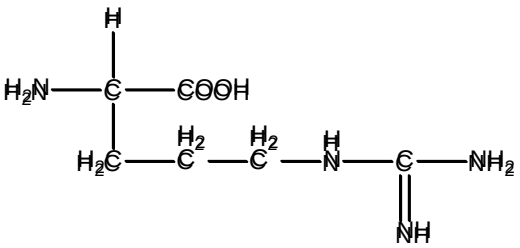
Isoleucine (Ile)



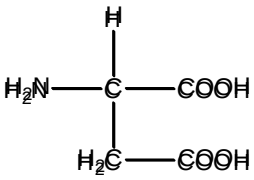
Glycine (Gly)



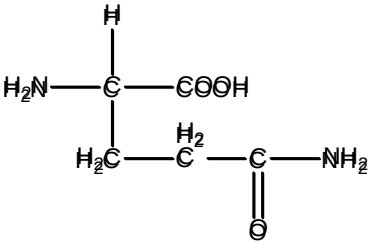
Asparagine (Asn)



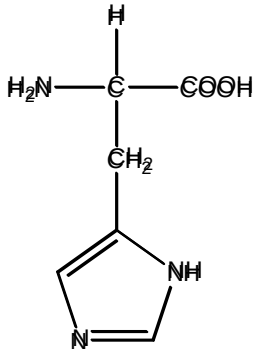
Arginine (Arg)



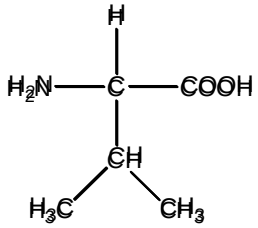
Aspartic Acid (Asp)



Glutamine (Gln)



Histidine (His)



Valine (Val)

- oooOooo -